

Titrimetry

Like gravimetry, this method is used for the quantitative determination of major constituents when high accuracy and precision better than 0.5 to 1% is required. It is often used as a standardization technique for other quantitative methods.

Principle of Technique

The sample solution containing an analyte reacts with a metered volume of a previously standardized titrant solution. The stoichiometric, complete reaction (i.e., end point) is detected by a color change or a change in potential indicated by a pair of electrodes. Both manual and computer-controlled titrations are possible.

Samples

Form. Solids (metals, ceramics, glasses, organic compounds, and mixtures) must be entirely dissolved; both aqueous and nonaqueous solutions can be titrated.

Size. A quantity sufficient to contain at least 2 to 3 mg of analyte per determination is needed.

Preparation. Solutions may be analyzed as received; solids require dissolution.

Limitations

Titrimetry is applicable primarily to elements in the middle of the periodic table: the actinides, halides, organic nitro compounds, and other compounds that are oxidizable or reducible in aqueous solution. It is not recommended for trace or minor impurity analysis because relatively large sample amounts may be required. Some determinations require the prior separation of the analyte from the sample matrix.

For inorganic constituent analysis, organics must be completely destroyed. A qualitative knowledge of sample composition is required in order to limit interferences.

Estimated Analysis Time

0.5 to 1 h per analysis is required after sample dissolution and preparation.

Capabilities of Related Techniques

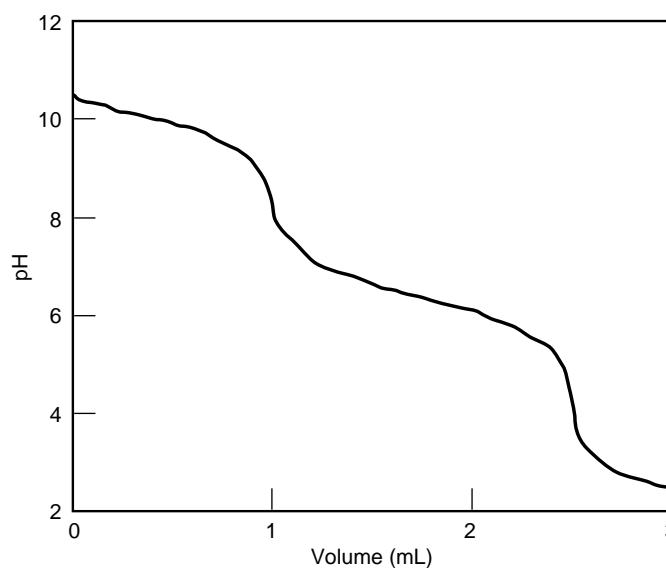
Among techniques with comparable accuracy and precision, titrimetry and gravimetry are generally applicable to the same types of samples. However, they require a larger quantity of analyte and may be more or less selective.

Coulometry can be used for smaller samples. It is comparable in accuracy and precision, and may be more selective but more complicated operationally.

Controlled-potential electrolysis can be used as a separation procedure preceding other measurement techniques and as a chemical synthesis technique.

Examples of Applications

- Determination of water by Karl Fischer titration.
- Measurement of high concentrations of metals in organic materials and metal alloys.
- Determination of acid and base concentrations in aqueous solutions.
- Determination of equivalent weights of amines.
- Measurement of halides in organic compounds.
- Standardization of elemental solutions for nuclear chemistry detectors.
- Determination of boron in weapons materials by mannitol titration.



Titration of 10 mL of a mixture of 0.01M Na_2CO_3 and 0.005M NaHCO_3 with 0.1M HCl .

Voltammetry and polarography measure electrolysis current-potential characteristics of solutions and are more suitable for minor constituent and trace analysis.

The various molecular spectroscopy methods (UV-visible spectrophotometry, Fourier transform infrared, Raman) and ion-selective electrode measurements can be substituted in many cases. These methods are generally less accurate and precise, but the results can often be improved by adding a titration step. Atomic spectroscopy methods like DC-arc optical

emission spectroscopy, inductively-coupled-plasma emission spectroscopy, DC-plasma optical emission spectroscopy, atomic absorption spectrometry, and x-ray fluorescence spectrometry can be used when speciation is unimportant, although again, these methods are usually less accurate and precise.

Ion chromatography (IC) is primarily applicable to anions where it approaches titrimetry in precision. IC may yield information about constituents in the sample other than the analyte, and is usually the preferred multianion, multiple sample technique.